

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: C.P. Kelkar, et al.	Art Unit: 1764
Serial No: 10/763,812	Examiner: Singh, Prem C.
Filing Date: January 23, 2004	
Title: <i>NOx Reduction Composition for Use in FCC Processes</i>	Atty. Docket No.: 4959

**APPEAL BRIEF**

Commissioner of Patents  
and Trademarks  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

This is an appeal from the Final Rejection of claims 17-23, and 25-29,  
dated April 15, 2008.

**REAL PARTY IN INTEREST**

The real party in interest of this application is BASF Catalyst, L.L.C.

**RELATED APPEALS AND INTERFERENCES**

There are no related Appeals or Interferences.

### STATUS OF THE CLAIMS

Claims 17-23 and 25-29, the only claims remaining in this application, have been Finally rejected and are being appealed.

### STATUS OF AMENDMENTS

No Amendment or Response was filed under 37 CFR 1.116.

### SUMMARY OF CLAIMED SUBJECT MATTER

Catalytic cracking of heavy petroleum fractions is one of the major refining operations employed in the conversion of crude petroleum oils to useful products such as the fuels utilized by internal combustion engines. In the fluidized catalytic cracking processes, high molecular weight hydrocarbon liquids and vapors are contacted with hot, finely-divided, solid catalyst particles, in a fluidized bed reactor and maintained at an elevated temperature in a fluidized or dispersed state for a period of time sufficient to effect the desired degree of cracking to lower molecular weight hydrocarbons of the kind typically present in motor gasoline and distillate fuels. In the catalytic cracking of hydrocarbons, some nonvolatile carbonaceous material or coke is deposited on the catalyst particles. The catalyst which has become substantially deactivated through the deposit of coke is continuously withdrawn from the reaction zone. This deactivated catalyst is conveyed to a stripping zone where volatile deposits are removed with an inert gas at elevated temperatures. The catalyst particles are then reactivated to essentially their original capabilities by substantial removal of the coke deposits in a suitable regeneration process. Regenerated catalyst is then continuously returned to the reaction zone to repeat the cycle (page 1, line 17- page 2, line 5).

Catalyst regeneration is accomplished by burning the coke deposits from the catalyst surfaces with an oxygen containing gas such as air. The combustion of these coke deposits can be regarded, in a simplified manner,

as the oxidation of carbon and the products are carbon monoxide and carbon dioxide. When sulfur and nitrogen containing feedstocks are utilized in the catalytic cracking process, the coke deposited on the catalyst contains sulfur and nitrogen. During regeneration of such coked deactivated catalyst, the coke is burned from the catalyst surface and results in the conversion of sulfur to sulfur oxides and nitrogen to nitrogen oxides (NO<sub>x</sub>), (page 2, lines 6-14).

The present invention encompasses the discovery that certain classes of compositions are very effective for the reduction of NO<sub>x</sub> gas emissions in FCC processes. Moreover, such compositions have unexpectedly improved hydrothermal stability over prior art compositions. The process of NO<sub>x</sub> reduction as in the invention of claim 17 is characterized as contacting a hydrocarbon feedstock during fluid catalytic cracking with a cracking catalyst and a NO<sub>x</sub> reduction composition comprising (i) mixed oxides of cerium and zirconium, (ii) optionally with an oxide of an additional rare earth other than cerium and (iii) at least one transition metal oxide selected from a metal of Group Ib or IIb of the periodic table (page 4, line 10- page 5, line 2). The NO<sub>x</sub> reduction composition contains at least 70 wt % of the ceria-zirconia (original claim 30).

Preferably, the mixed oxide of ceria and zirconium contains at least 20 wt.% cerium oxide and at least 15 wt.% zirconium oxide (claim 23, supported at page 5, lines 2-3). Further, the composition includes a lanthanide other than ceria, such as La, Nd, Pr or mixtures thereof (claims 26 and 27, supported at page 4, lines 31-32 and by Examples 4 and 5).

GROUND OF REJECTION TO BE REVIEWED ON APPEAL

1. Claims 17-23, and 25-29 have been Finally rejected under 35 U.S. C. 103(a) as being unpatentable over Peters et al. (U.S. Patent No. 6,379,536) in view of Aubert et al. (U.S. Patent No. 6,214,306). With respect to claim 17, the Examiner applies Peters as disclosing a process for NO<sub>x</sub> control in an FCC process by using a composition with the cracking catalyst that comprises (i) an acidic oxide support, (ii) an alkali/alkaline earth metal, (iii) a transition metal oxide having oxygen storage capability, and (iv) a transition metal selected from Group IB and/or Group IIB, column 1, lines 53-62, and claim 12. The Examiner admits that Peters does not disclose (i) mixed cerium and zirconium oxide in the NO<sub>x</sub> reduction composition used in the claimed invention. However, Peters uses ceria, column 2, lines 50-52 and further discloses, "Other non-stoichiometric metal oxides having known oxygen storage capability may also be used", Column 2, lines 52-53. Aubert is applied as disclosing a composition based on zirconium and cerium oxides and its use in NO<sub>x</sub> reduction. Aubert further discloses that the composition comprises (i) zirconium oxide and cerium oxide and it is provided in the form of pure solid solution of cerium oxide in zirconium oxide, column 1, lines 30-35. Aubert also discloses that the composition of the invention can be used in the catalysis of various reactions such as hydrodenitrification, cracking, hydrocracking, etc., column 7, lines 50-60. Aubert also discloses that zirconium oxide and cerium oxide today appear as two particularly important and advantageous constituents in multifunctional catalysts, column 1, lines 10-17.

The Examiner concludes that since both Peters and Aubert disclose a similar NO<sub>x</sub> reduction composition in a catalytic cracking process, and also since zirconium is known for its oxygen storage capability, it would have been obvious to one skilled in the art at the time the invention was made to modify Peters invention and add (i) a mixed zirconium oxide and cerium oxide as suggested by Aubert into the composition of Peters for an enhanced NO<sub>x</sub> reduction capability. It would also have been obvious to combine the Peters and Aubert inventions and specify the ratio of cerium plus zirconium oxide and other components of the NO<sub>x</sub> reduction composition given by Peters. With

respect to claims 18-22, 25, 28 and 29, Peters is applied as disclosing the claimed limitations. The Examiner admits that the Peters invention does not disclose the cerium and zirconium oxide contents as recited in claim 23. Aubert discloses in column 3, lines 10-25 that expressed in the form of oxides, the composition, according to the invention, generally contain at least 40% by weight zirconium and at most 60% by weight cerium. Thus, it would have been obvious to one skilled in the art at the time the invention was made to modify Peters' invention and use a Zr/Ce ratio as claimed, for a better NO<sub>x</sub> reduction composition. With respect to claims 26 and 27, Peters' invention discloses, "The transition metal oxide having oxygen storage capability may be any transition oxide having oxygen storage capability similar to that of ceria." (Column 2, lines 47-49). Since Peters suggests using any transition metal oxide similar to ceria and Aubert discloses using lanthanum as a doping element in the NO<sub>x</sub> reduction composition, column 2, lines 47-57, it would have been obvious to one skilled in the art at the time the invention was made to modify Peters invention and use lanthanum oxide in place of ceria for similar performance in the NO<sub>x</sub> reduction. Aubert further discloses, "Mention may more particularly be made of yttrium, lanthanum, neodymium, praseodymium, europium, and samarium." (Column 2, lines 55-57).

2. Claims 17-23 and 25-29 have been Finally rejected on the ground of nonstatutory obviousness-type double patenting as being unpatentable over claims 1-9 of U.S. Patent No. 6,852,298. The Examiner has stated that although the conflicting claims are not identical, they are not patentably distinct from each other because the '298 claims have an acidic support and only cerium oxide as one component. The present application does not claim an acidic support and claims a mixed oxide of cerium and zirconium. Since the support material does not play an active role in the NO<sub>x</sub> reduction process during FCC operation, and since zirconium and cerium appear to be two particularly important and advantageous constituents in multifunctional catalysts for NO<sub>x</sub> reduction, it would have been obvious to one skilled in the art at the time the invention was made to modify the '298 claims to eliminate the acidic oxide support and include zirconium with cerium for an enhanced NO<sub>x</sub> reduction.

## ARGUMENT

1. The rejection of claims 17-23 and 25-29 under 35 U.S.C. 103 as being unpatentable over Peters, et al. (U.S. 6,379,536) in view of Aubert, et al. (U.S. 6,214,306).

Peters discloses a NO<sub>x</sub> reduction composition containing an alkaline metal or alkaline earth metal which is not part of the claimed invention, a transition metal oxide having oxygen storage capability such as ceria, and a transition metal selected from Group 1b and/or 2b which is part of the claimed invention. The Examiner is correct in that Peters does not disclose the use of a mixed oxide of cerium and zirconium. The Examiner utilizes Aubert to meet the limitation of a mixed oxide of cerium and zirconium and suggests it would be obvious to replace the cerium oxide of Peters with the solid solution of zirconium oxide and cerium oxide of Aubert, inasmuch as Aubert discloses that these materials can be used in catalysis. Essentially the Examiner is stating that ceria and a mixed oxide of cerium and zirconium, are equivalent and/or the broad suggestion that the solid solution of cerium oxide and zirconium oxide in Aubert would have known advantages in removing NO<sub>x</sub> in an FCC process. It is these latter conclusions, explicit or implied by the Examiner over which the Appellants strongly disagree. There is no suggestion in any of the applied references that ceria and a mixed oxide of cerium and zirconium are equivalent. More importantly, Aubert does not disclose the advantages that Appellants have found using a mixed oxide of cerium and zirconium in an FCC process for NO<sub>x</sub> reduction. While Aubert discloses that his cerium and zirconium mixed oxide or solid solution can be used in a wide variety of catalytic operations, the patent does not otherwise suggest that this material could be a replacement for or in addition to ceria in a NO<sub>x</sub> reduction FCC catalyst as in Peters. Importantly, Appellants have found that the mixed oxide of cerium and zirconium yields improved stability in FCC processing over ceria or zirconia alone. The Honorable Board of Appeals is kindly invited to Table 1 of the present application as a showing of the unexpected surface area retention ("SA retention %") and NO retention after catalyst steaming

found using a mixed cerium-zirconium oxide. The catalyst steaming is a well known process which represents catalyst aging during FCC processing. Thus, it is Appellants position that while mixed oxides of cerium and zirconium with other optional oxides or rare earths have found extensive use in automotive exhaust catalysts, the stability which Appellants have found in FCC processing has not been known prior to this invention, and is certainly not suggested in the broad recitation of possible useful catalysis processes disclosed in Aubert. Aubert does not remotely suggest the results which are shown in Table 1 of the present application. Accordingly, the use of a cerium/zirconium mixed oxide as a substitute for ceria or as an additive in the NOx reduction catalyst of Peters yields results which are unexpected from a reading of the applied art. The Examiner has simply ignored the improved and unexpected results which have been found in a catalyst for the specific claimed FCC environment. It is believed that the claimed method of reducing NOx emissions utilizing the claimed catalyst yields results which are not expected from the applied prior art either singularly or in combination.

The Examiner argues that there is no equivalence between ceria as in Peters and the ceria-zirconia mixed oxide of Aubert, but still concludes that one skilled in the art would modify Peters and use a mixture of cerium oxide and zirconium oxide for enhanced NOx removal. The Examiner relies on Aubert's discussion of the use of the claimed mixed oxide for NOx removal in "three way" auto exhaust catalysts. The Aubert patent is not at all specifically concerned with NOx reduction. The patent states in a paragraph at column 7, lines 50-63 that the catalytic system has a great many applications and absurdly lists every catalytic process imaginable where ceria-zirconia can be used. While this list may suggest an "obvious to try" standard, one of ordinary skill in the catalyst art would have no way of predicting how the mixed oxide would perform in any of the listed processes. There is no specific reference in Aubert to NOx reduction in an FCC process wherein the mixed oxide of cerium and zirconium has improved stability over ceria or zirconia alone, as shown in Table 1 of the present application.

The use of a mixed oxide of cerium and zirconium for “three way” automotive catalysts is not disputed by Appellants. In fact, at page 5, lines 8-15 of the instant specification, it is specifically stated that mixed oxides of cerium and zirconium, with other optional oxides of rare earths, have found extensive use in automobile exhaust applications. The gaseous environment of the automobile exhaust is not remotely the same as the mixed liquid and gaseous environment and substantially harsher conditions of temperature and pressure in FCC processing of a hydrocarbon feedstream. What Aubert does not disclose or suggest is that under the harsh FCC conditions, the ceria-zirconia solid solution will yield improved stability as found by Appellants relative to ceria alone, such as in the primary reference to Peters. The Examiner has dismissed this argument as non-persuasive indicating that the combined teachings of Peters and Aubert will inherently have all the claimed advantages shown in Table 1. The use of inherency in a combination of references is improper since once the combination is suggested, the combination will always yield the results found, and which are not otherwise disclosed or suggested in the applied art prior to the suggested combination. It is the results shown in Table 1 which are unexpected and which have been found by Appellants only, not by Peters and not by Aubert. Accordingly, the combination of ceria and zirconia of Aubert for replacing the ceria of Peters yields an unexpected result, which is the capstone of unobviousness.

The Examiner appears to further argue that the steaming conditions used to generate the data for aforementioned Table 1 is suggested in Aubert, which discloses typical steps involved in making the catalyst composition including thermal hydrolysis, washing, drying, and calcining. These typical catalyst forming steps are not remotely the same or equivalent to the steaming steps used in Table 1 to simulate catalyst aging in FCC processing. Accordingly, it is again stated that the secondary reference to Aubert simply does not suggest the improved stability during FCC processing that the Appellants have found using a mixed oxide of cerium and zirconium with respect to ceria used in the primary reference.



2. The rejection of claims 17-23 and 25-29 on the ground of non-statutory obviousness type double patenting as unpatentable over claims 1-9 of U.S. Patent No. 6,852,298.

The instant claims are not at all claiming the same subject matter as claims 1-9 of U.S. 6,852,298. While the '298 patent and the instant claims are directed to reducing NOx emissions in an FCC process, the catalyst compositions for doing so are different. In the '298 patent, a mixture of cerium oxide and an oxide of a lanthanide series element other than ceria is claimed and the ratio of the cerium oxide to the other lanthanide oxide is specifically set forth. The presently claimed invention is not directed to ceria but is directed to a solid solution or a mixed oxide of cerium and zirconium. Data in the application clearly indicates an improvement of the mixed oxide of cerium and zirconium over ceria alone. Accordingly, it would not be obvious to substitute a mixed oxide of cerium and zirconium for the ceria alone of the patent. Inasmuch as the claimed invention of the present application and the '298 patent are directed to the use of different compositions, and inasmuch as Appellants have shown unexpected results with respect to a mixed oxide of cerium and zirconium relative to ceria alone, the obviousness type double patenting rejection is simply improper.

The Examiner argues that the ratio of lanthanide element to ceria could be modified so that the lanthanide element is negligible. The Examiner improperly relies on the specification of the '298 patent to draw such a conclusion. The fact remains that the claims of the '298 patent do not suggest a ceria-zirconia mixed oxide and instead require a specific ratio of ceria to other lanthanide, which ratio is not part of the instant claimed invention.

CONCLUSION

For the above stated reasons it is believed that the Final Rejection of claims 17-23 and 25-29 is in error and Appellants respectfully request a reversal of the Final Rejection and allowance of claims 17-23 and 25-29.

Respectfully submitted,

Date: September 4, 2008

/Stuart D. Frenkel/

Stuart D. Frenkel  
Reg. No. 29,500

Frenkel & Associates, P.C.  
3975 University Drive, Suite 330  
Fairfax, VA 22030  
Telephone: (703) 246-9641  
Facsimile: (703) 246-9646

## CLAIMS APPENDIX

The claims in this Appeal are:

17. A method of reducing NO<sub>x</sub> emission during fluid catalytic cracking of a hydrocarbon feedstock into lower molecular weight components said method comprising contacting a hydrocarbon feedstock with a cracking catalyst suitable for catalyzing the cracking of hydrocarbons at elevated temperature whereby lower molecular weight hydrocarbon components are formed in the presence of a NO<sub>x</sub> reduction composition, wherein said NO<sub>x</sub> reduction composition comprises a (i) mixed oxide of cerium and zirconium, (ii) optionally, at least one oxide from the lanthanide series other than cerium and (iii), an oxide of a transition metal selected from Groups Ib and IIb of the Periodic Table, said mixed oxide (i) is present in amounts of at least 70% by weight relative to the total of (i), (ii), and (iii) said NO<sub>x</sub> reduction component being present in a sufficient NO<sub>x</sub> reducing amount.

18. The method of claim 17 wherein said cracking catalyst and NO<sub>x</sub> reduction composition are separate particles.

19. The method of claim 17 wherein said cracking catalyst and NO<sub>x</sub> reduction composition are present as an integral combination of the cracking catalyst component and the NO<sub>x</sub> reduction composition component in a single particle.

20. The method of claim 17 wherein said cracking catalyst is fluidized during contact with a hydrocarbon feedstock.

21. The method of claim 17 further comprising recovering used cracking catalyst from said contacting step and treating said used catalyst under conditions to regenerate said catalyst.

22. The method of claim 17 wherein said hydrocarbon feedstock contains at least 0.1 wt % nitrogen.

23. The method of claim 17 wherein said mixed oxide (i) contains at least 20 % cerium oxide by weight and at least 15% zirconium oxide by weight.

25. The method of claim 17 wherein said at least one oxide of a transition metal (iii) is copper oxide or silver oxide.

26. The method of claim 17 wherein said NO<sub>x</sub> reduction component includes positive amounts of component (ii).

27. The method of claim 26 wherein (ii) comprises oxides of La, Nd, Pr, or mixtures thereof.

28. The method of claim 18 wherein components (i), (ii), and (iii) comprise at least 40 weight % of said NO<sub>x</sub> removal composition.

29. The method of claim 18 wherein components (i), (ii), and (iii) comprise at least 55 weight % of said NO<sub>x</sub> removal composition.

EVIDENCE APPENDIX

Not applicable.

RELATED PROCEEDINGS APPENDIX

Not applicable.